

MICROSTRUCTURE AND THERMAL CONDUCTIVITY OF THERMAL BARRIER COATINGS PROCESSED BY PLASMA SPRAY AND PHYSICAL VAPOR DEPOSITION TECHNIQUES

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ABSTRACT

The temperature dependence of the thermal conductivity of multilayer coatings made by a plasma spray technique as well as some coatings made by physical vapor deposition (PVD) was investigated. The multilayer coatings consisted of a varying number of layers of Al_2O_3 and ZrO_2 stabilized by 8% Y_2O_3 . Plasma sprayed coatings exhibited a large reduction in thermal conductivity at all temperatures when compared to the bulk monolithic materials. This reduction was found to be due to porosity as well as thermal resistance brought about by interfaces in the coatings. A comparable reduction in thermal conductivity was achieved in monolithic ZrO_2 as well as in a composite coating deposited by the PVD technique. Microstructural factors that may be responsible for this reduction are discussed.

INTRODUCTION

Improvements in the efficiency of gas turbine require the highest operating temperatures possible. Because the Ni-base superalloys used as turbine materials rapidly lose strength and oxidize above 1000°C, a reduction in service temperature is often accomplished by the use of thermal barrier coatings [1,2]. Traditionally, such coatings have been applied by plasma spray [1] or physical vapor deposition [2] onto turbine components with an intermediate NiCoCrAlY alloy bond coating to improve adherence and to reduce oxidation. The thermal conductivity of these coatings is sensitive to the deposition technique, microstructure, density, and interface thermal resistance between layers [3]. The general objective of this research was to examine the relationship between the coating microstructure and thermal conductivity. Specifically, the thermal conductivities of multilayer coatings involving alternating ZrO_2 and Al_2O_3 layers, deposited by plasma spray (PS) as well as the coatings deposited by physical vapor deposition (PVD) technique, were investigated. These configurations were expected to provide reduced thermal conductivity due to the interfaces present in these coatings.

EXPERIMENTAL PROCEDURE

Plasma sprayed coatings were obtained by spraying alternating layers of ZrO_2 and Al_2O_3 onto a 3mm thick superalloy substrate measuring 62.5mm X 12.5mm. Powders of ZrO_2 stabilized with 8% Y_2O_3 with an average particle size of about 10 μm and Al_2O_3 with an average particle size of about 5 μm were used. A Plasma Technik Spray system, with a single spray nozzle and dual powder feeder at the Thermal Spray Laboratory of the State University of New York, Stony Brook, NY, was used. Calibration sprays were performed to control the layer thickness during the actual multilayer spray deposition. The ZrO_2 and Al_2O_3 powders were alternately fed in to the spray gun, and deposition was carried out for a specified period, determined from the calibration trials and the required layer thickness. To determine if residual porosity could be closed by sintering, heat treatment of these coatings was performed at 1300°C for 50 hrs in a furnace under flowing argon. However, the coatings detached from the substrate as units after such a sintering heat treatment. Porosity levels were determined using measurements of coating mass and volume as well as by the point counting technique on micrographs.

PVD coatings were deposited using a proprietary PVD process. A monolithic ZrO_2 coating and a composite coating comprising of ZrO_2 and Al_2O_3 were deposited.

Thermal conductivity (TC) measurements were made by the Thermophysical Properties Research Laboratory of Purdue University, West Lafayette, IN, using the laser flash method. Details of this technique are available elsewhere [4]. TC measurements at room temperature and at various temperatures to 1000°C were performed. Measurements were made on the coatings with substrate in the as-sprayed condition, but only on the coatings in the detached condition after heat treatment.

RESULTS AND DISCUSSION

(a) Plasma Sprayed Coatings

The single layer Al_2O_3 and ZrO_2 PS coatings were designated as A1 and Z2, respectively. The multilayer coatings were identified as AZ11, AZ21, AZ41 and AZ81 in which the first number after Z identifies the number of alternating layers each of Al_2O_3 and ZrO_2 (AZ41 consists of 4 layers each of Al_2O_3 and ZrO_2). Microstructures of some of the coatings are shown in Fig. 1 and 2, for the as-sprayed condition and after heat treatment, respectively. The porosity levels in the coatings were: A1: 18.8%; Z2: 11.9%; AZ11: 15.5%; AZ21: 17%; AZ41: 12.7%; AZ81: 13.7%. While there appears to be no change in porosity in Al_2O_3 layers, a slight reduction in porosity in ZrO_2 layers after heat treatment can be seen.

The thermal conductivity data as a function of temperature are presented in Figs. 3 and 4 for coatings in the as-sprayed and in the heat-treated conditions, respectively. In Fig. 3, it can be seen that the thermal conductivity levels of monolithic as well as multilayer coatings are lower than that of dense materials. At temperatures <200°C, the TC levels of coatings and the monolithic ZrO_2 are comparable. On the other hand, the TC values are at least a factor of two lower than that of monolithic ZrO_2 at temperatures >200°C. The TC of Al_2O_3 coating is slightly higher than that of the other coatings. The TC levels of all the multilayer coatings average around the monolithic ZrO_2 coating, but are slightly lower than the trend calculated from the monolithic TC values on the basis of a series arrangement of alternate layers (for a bi-layer, $\lambda = \lambda_{\text{Al}_2\text{O}_3}\lambda_{\text{ZrO}_2} / (\lambda_{\text{Al}_2\text{O}_3}t_{\text{ZrO}_2} + \lambda_{\text{ZrO}_2}t_{\text{Al}_2\text{O}_3})$, in which λ is thermal conductivity and t is the thickness fraction of each layer). Also included in the figure is the TC for a bi-layer calculated using the dense TC values reported in the literature and accounting for the effect of porosity on thermal conductivity of each layer. The data for dense Al_2O_3 and ZrO_2 were taken from Refs. [5] and [6], respectively. The effect of porosity on thermal conductivity was incorporated using the relationship: $\lambda = \lambda_d [1 - P^{2/3}]$ (λ_d is the TC of dense material and P is the volume fraction of porosity). It can be seen that the measured TC data for multilayers are significantly lower than this value at all temperatures. This suggests that the reduction in thermal conductivity of plasma sprayed coatings can be explained only partially on the basis of the porosity of coatings, and that other microstructural factors are equally important.

The TC levels of all the coatings after heat treatment were significantly higher than those in the as-sprayed condition as shown in Fig. 4. It is to be noted that while the data for all the as-sprayed coatings showed a significant change with temperature, the TC data after sintering were largely temperature-independent. The thermal conductivities of the multilayer coatings are in agreement with the estimated bi-layer thermal conductivity using the data of monolithic coatings as well as the predictions based on the dense materials after accounting for the effects of porosity on thermal conductivity. In the latter, the porosity data of as-sprayed coatings were used in the calculation because there was only a small change in porosity during heat treatment.

These results indicate that several microstructural factors should be considered in understanding thermal conductivity changes after heat treatment. Porosity and thermal resistance at interfaces can significantly influence the thermal conductivity in solids [7,8].

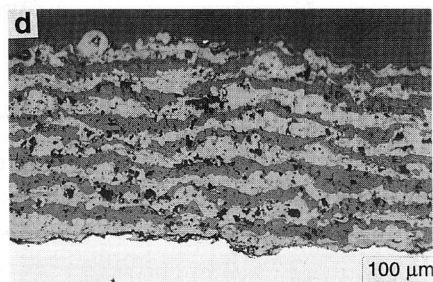
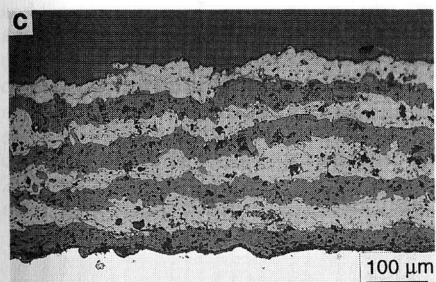
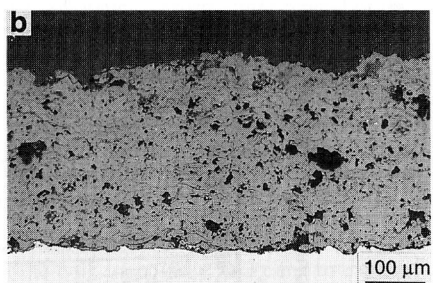
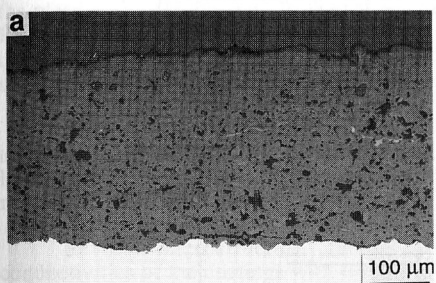


Fig. 1. Microstructures of plasma sprayed coatings in the as-sprayed condition. (a) A1, (b) Z2, (c) AZ41 and (d) AZ81.

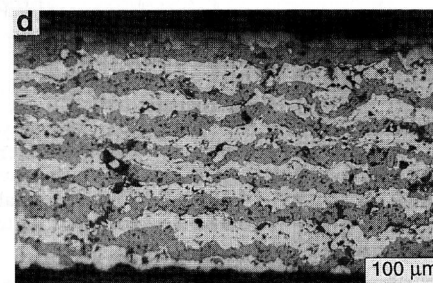
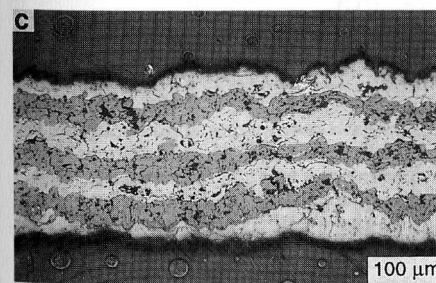
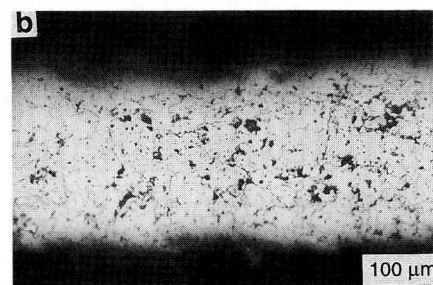
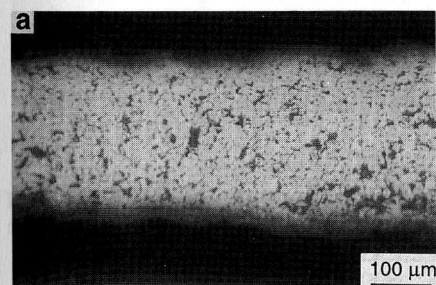


Fig. 2. Microstructures of plasma sprayed coatings after the heat treatment. (a) A1, (b) Z2, (c) AZ41 and (d) AZ81.

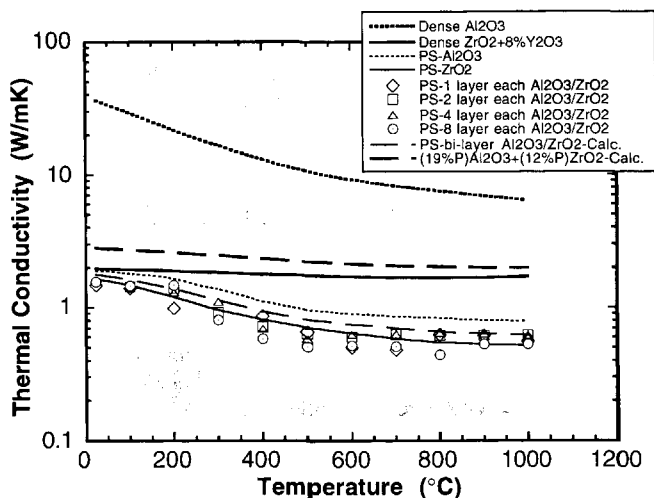


Fig. 3. Thermal conductivity of plasma sprayed coatings in the as-sprayed condition.

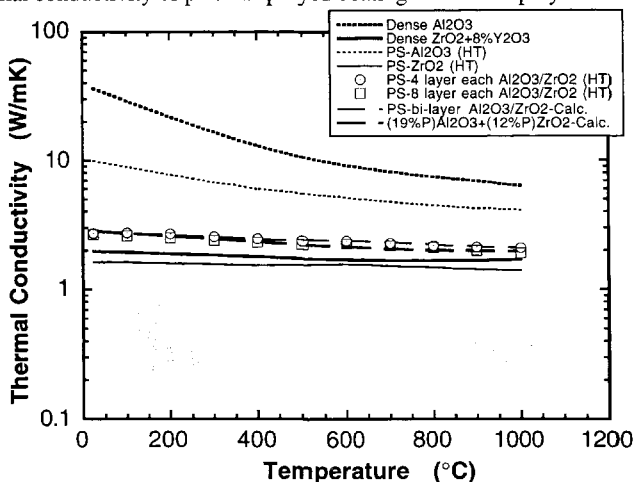


Fig. 4. Thermal conductivity of plasma sprayed coatings after heat treatment at 1300°C for 50 hrs. HT refers to the heat-treated condition.

Since porosity levels changed only a little, this is not a major factor. On the other hand, interfaces between the splats in thermal sprayed coatings have been suggested to contribute to reduced thermal conductivity due to the interface thermal resistance [3,8]. In addition, there are interlayer interfaces and the interface between the coating as a unit and the substrate. Thus, although the bulk of the reduction in thermal conductivity appears to be due to an interface-type effect, at this stage it is not possible to determine the specific contributions from the different interfaces.

(b) PVD Coatings

Microstructures of the PVD coatings were very different from those deposited by

the plasma spray technique. Both coatings exhibited a columnar microstructure typical of the PVD process [9,10]. Fig. 5 shows the microstructures of monolithic ZrO_2 coating as seen in the optical and scanning electron microscopes. The microstructures of the composite coating are not shown here because of its proprietary nature.

Thermal conductivity data for the PVD coatings are presented in Fig. 6. At temperatures above 500°C , both coatings have similar thermal conductivity levels. However at lower temperatures, the composite coating is seen to have a lower thermal conductivity, the magnitude of this difference increasing at lower temperatures.

Several microstructural factors must be considered to interpret the thermal conductivities of the coatings with respect to that of the bulk monolithic ZrO_2 and to explain the differences between the coatings themselves. First, the differences between bulk material and the coatings need to be examined. A preliminary X-ray diffraction study indicated that the amount of monoclinic ZrO_2 (M- ZrO_2) in both the coatings was negligible and the coatings consisted entirely of tetragonal ZrO_2 (T- ZrO_2) phase. However, the reference bulk ZrO_2 consisted of a significant amount of M- ZrO_2 in addition to T- ZrO_2 . Additionally, strong (200) and (111) textures were observed in the coatings. Hence, both the absence of M- ZrO_2 phase and the presence of anisotropy in coatings may explain part of the reduction in the thermal conductivities of both coatings compared to that of the bulk material. Since the effects of M- ZrO_2 versus T- ZrO_2 phase proportion and crystal orientation on thermal conductivity are not clear, these effects could not be quantitatively assessed at present.

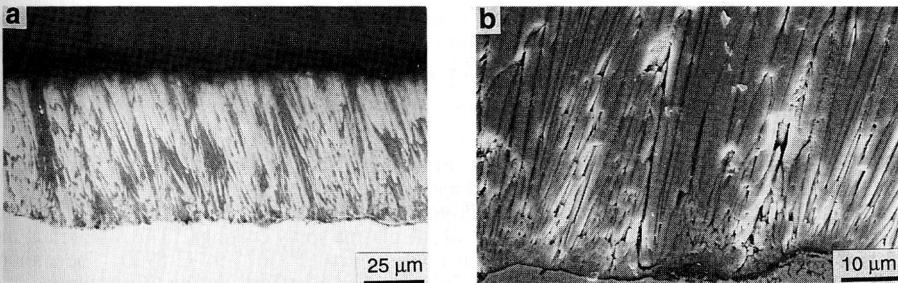


Fig. 5. Microstructure of ZrO_2 coating deposited by the PVD technique as seen in (a) optical microscope and (b) scanning electron microscope.

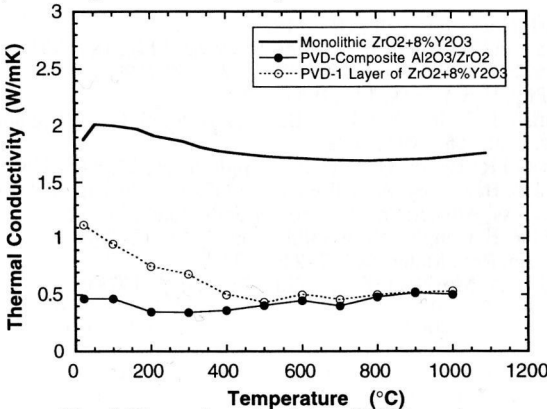


Fig. 6. Thermal conductivity of PVD coatings.

The microstructure of the composite coating differs from that of the monolithic coating in several aspects. First, the composite coating had a (111) texture compared to a (200) texture in the monolithic coating. Secondly, the composite had unique microstructural arrangement that differed from the monolithic coating. X-ray diffraction indicated that the Al_2O_3 was present in an amorphous form. Further research is necessary to understand the impact of these differences and other factors on the thermal conductivity of the composite coatings.

CONCLUSIONS

1. The thermal conductivity of the plasma sprayed multilayer coatings comprising alternating $\text{Al}_2\text{O}_3/\text{ZrO}_2$ layers was comparable to the monolithic ZrO_2 coating made by the same technique. This similarity appears to be due to porosity and the thermal resistance due to interfaces in the microstructure.
2. After heat treatment, the effect of interface thermal resistance on conductivity was absent. However, because the coatings detached after heat treatment, it is not clear whether the elimination of thermal resistance was due to the increased contact between internal interfaces or the elimination of the interface between the coatings as units and the substrate.
3. The thermal conductivity of the PVD coatings was comparable to that of the plasma sprayed coatings although their microstructures were entirely different. Such a large reduction in thermal conductivity may be due to the proportion of M- ZrO_2 versus T- ZrO_2 as well as the presence of anisotropy in the coatings.
4. The PVD composite $\text{Al}_2\text{O}_3/\text{ZrO}_2$ coating showed a significantly lower thermal conductivity compared to that of the monolithic ZrO_2 coating at temperatures below 500°C . This may be due to its unique microstructural characteristics, compared to monolithic coating.

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